Development of advanced coating process on NMC with Li-ionic conductive materials

Undergraduate Honors Thesis

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Abstract

As the hybrid electric vehicles (HEV) and electric vehicles (EV) occupies more in the automobile market, the battery industry faces enormous challenge since the demands for high-performance batteries increase fast by time. The currently used batteries are typically lithium-ion batteries due to its high energy density. There are still significant needs to improve the cycle lives and abuse tolerance of Li-ion batteries, especially for EV applications. In this regard, protecting the surface of cathode, which is the most expensive components in Li-ion batteries, will be an effective approach to extend the life of battery cells. This research aims to improve battery performances by implementing $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP), Li-ionic conductive material, in the cathode by using different methods: powder mixing and electrode plating methods. For the powder mixing method, LATP and $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC) powder were mixed with two compositions: NMC: LATP = 1:1 or 3:1 wt. ratio. For the electrode plating method, the LATP slurry was coated on the pre-coated NMC cathode. Here, thickness of the plated LATP layer on top of the NMC cathode was controlled to investigate its impact on the Li-ion battery performance. The results showed that both methods offer the improved cycle-ability and/or rate-capability.

Acknowledgments

As an undergraduate student, I am always not qualified enough for the research that is so professional like this. Huge thanks to Dr. Kim Jung Hyun, my research advisor, who gave me such trust to conduct this research. All the works I have completed come from the knowledge and tutorial I received from my Dr. Kim and senior researchers in the Energy Innovation laboratory. I owe a huge thank to all the researchers in this lab and managers that allow me to use the equipment in the lab.

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Introduction

Lithium-ion batteries (LIB) are the most commonly used rechargeable batteries for providing high and long-lasting energy nowadays. It consists of three advantages compared to the other types of batteries which are 1. high energy density, 2. low memory effect, and 3. low self-discharge. [1–3]And the price for making LIB is not so expensive that it could still be afforded by industry to make profits. The main structure of a LIB is Cathode, Anode, electrolyte, and separator.

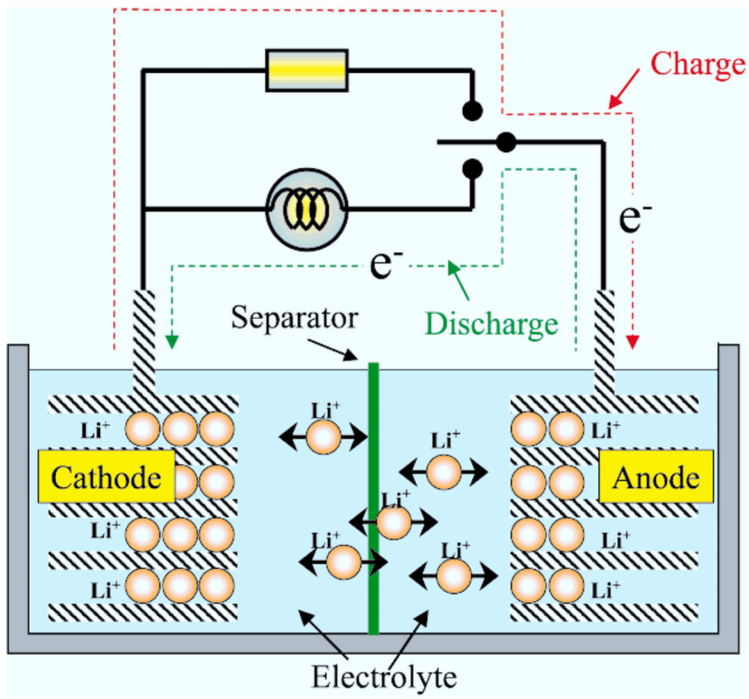

Figure 1. schematics of the principles in the Lithium-ion battery (LIB)[4]

The cathode materials are typically made from the Transition metal oxide to be able to hold the Lithium ions for reciprocal transfer between the cathode and the anode. So far, the NMC which is $LiNi_xCo_yMn_{1-x-y}O_2$ is one of the most commonly used material to form cathode.[5]

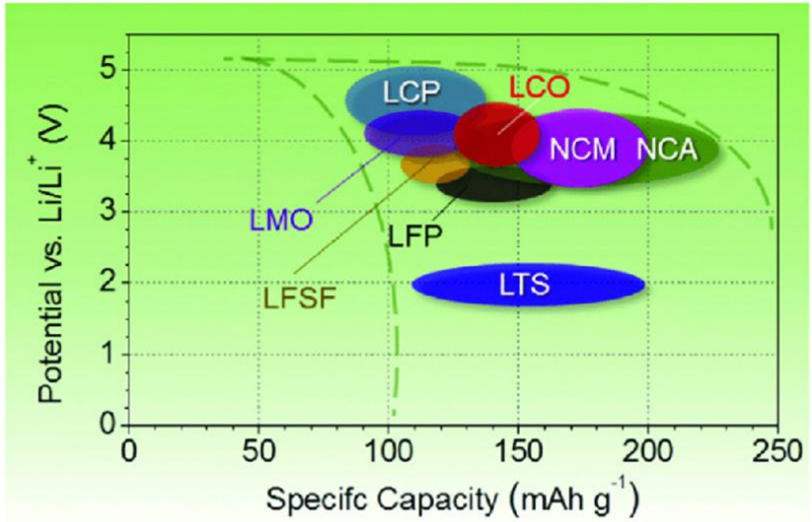

Figure 2. Potential versus specific capacities of the cathode materials in LIB.[6]

As Figure 2 shows, the NCM is the NMC we use, it consists with high potential and high specific capacity and it is far more economically friendly than the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) which is in theory the most extraordinary material for cathode making.[7] But NMC also has one flaw: it consists with a significantly low lithium-ionic conductivity which is around 10^{-10}~10^{-12} S/cm. The low ionic conductivity of NMC may be the main contributor to its disadvantages. Therefore, the research will focus on adding in another material with high lithium-ionic conductivity to ease the effect brought from the low ionic conductivity and therefore improve the performance. The material the research chose to investigate is $(Li_{1+x}Al_XTi_{2-x}(PO_4)_3)$, which is also called LATP for convenience. LATP is a material with high lithium-ionic conductivity at and above the room temperature (25℃, 298K).[8,9]

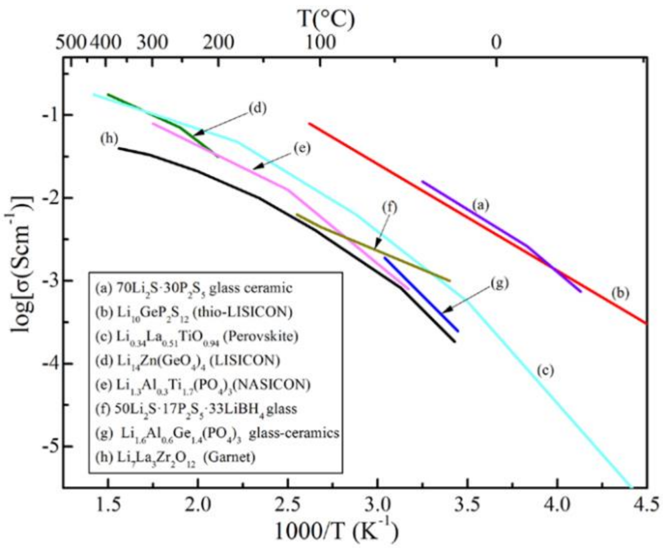

*Figure 3. Ionic conductivity of regularly used materials*10

As the figure 3 shows, when the temperature is larger than 298 K, the ionic conductivity of LATP is in a definite advantage compared to the other materials, therefore LATP will be the most optimum objective for this research.

Focus of Thesis

The research project aims to discover the effect that the LATP as coating material will have on the NMC cathode. The research will also validate different ways of coating with LATP material on the NMC cathode so that an optimum coating method could be found. There are mainly two ways of coating methods considered: mixing and plating. Before the experiment, the LATP particles will be synthesized and then the particles will be checked with XRD to compare with the pattern of commercial LATP to ensure the LATP is synthesized correctly. There are in total three conditions conducted during the experiment: (1). Mixing NMC powder with LATP powder in wt. ratio 1:1. (2). Mixing NMC powder with LATP powder in wt. ratio 3:1. (3). Plating LATP layer on NMC cathode. The component of the cathode made are uniform: 85% of active materials (NMC-LATP mixture or pristine NMC), 7.5% of carbon black (super D) and 7.5% of polymer binder.

Significance of Research

As the demand for high-performance lithium-ion batteries grows more rapidly among the market since EVs are becoming more popular. The coating is by far the most optimum way to improve the battery performance since the material needed for coating is much cheaper than the battery materials and it does not require much modification on the structure of the batteries. The coating mechanism is also compatible with the solid-state batteries, meaning that it will remain valuable for a very long time through the next generation of Li-ion batteries.

Experiments

Preparation of samples

Due to the various conditions involved in the experiments, the preparation of the samples is extremely crucial for the whole process. The NMC used in the research is the same as the ones that are commercially used. The solid electrolyte $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) powder was prepared using a sol-gel method.[6] Lithium nitrate ($LiNO_3$) and titanium (IV) butoxide ($Ti(C_4H_9O)_4$) was dissolved in ethylene glycol ($C_2H_6O_2$). Within the stirring condition, aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and citric acid ($C_6H_8O_7$) were added to the solution. The solution was then heated at 170 ℃ until the viscous gel was formed. The resulting gel was calcined at 300 ℃, followed by sintering at 850 ℃ for 5 h to produce the LATP powders. To reduce the particle size, the LATP powder is placed in the bottle and the ceramic balls are also added in, the bottle was then being rotated for a day to let enough collisions between ceramic balls and LATP particles happen.

Material Characterization

After the synthesis, X-ray Diffraction (XRD) pattern for powder samples were obtained using Rigaku SmartLab XRD (Cu Kα radiation) to identify the phases. The morphologies were observed by the scanning electron microscope (SEM).

Improving method I: mixing

The first coating method considered in this research is mixing, the process is adding a certain amount of the LATP to the commercially used cathode material – NMC. To investigate the optimum amount of the LATP in the NMC to boost the performance of the battery, three conditions are considered

Condition 1	Pristine NMC
Condition 2	NMC: LATP = 3:1
Condition 3	NMC: LATP = 1:1

Table 1. conditions for mixing method

The mixture is then mixed with additional materials to make cathode.

The proportions of materials are listed in terms of wt.%:

- Active material (NMC-LATP mixture) 85%
- Carbon black (added to reinforce conductivity) 7.5%
- Polymer binder (added to stick materials together) 7.5%

The materials are then dissolved in an organic solution called NMP to form a mud-like liquid, this is mainly for the extension of the polymer binder since the binder was added in the state of solid particles which have a compact and twisted structure, while to function as a binder, it needs to be dissolved first to let the polymer structure extend. The dissolved mud-like liquid is afterward plated on an aluminum foil. The foil will be put in the oven which consists of 80℃ inside and being heated overnight to evaporate the organic solution.

Improving method II: plating

The second coating method the research investigated is plating. To conduct plating, instead of mixing the NMC particles and LATP particles, the researcher chose to plate the pristine NMC using the same condition described in the previous method:

- Active material (Pristine NMC) 85%
- Carbon black (added to reinforce conductivity) 7.5%
- Polymer binder (added to stick materials together) 7.5%

The pristine NMC Cathode is then placed in the oven overnight to evaporate the remaining organic solution to be prepared to be plated.

The LATP plating layer is processed next. Before being dissolved in the NMP solution, another compound called PAA is added into the LATP particles to ensure a homogenous plating layer which consists of uniform thickness is made. The mixture of LATP and PAA particles are then dissolved in NMP to form a mud-like solution and being plated on the pristine NMC cathode that was already made. The reprocessed cathode was then put in oven overnight again to evaporate any remaining organic solution.

Figure 4, pristine NMC cathode without LATP coated

Figure 5, LATP plated NMC cathode

Electrochemical evaluation

Electrochemical properties are evaluated by fabricating CR2032 coin-type cells. The cells are assembled using the NMC cathode material and they are put in a cycler to be tested under different conditions, the first test is cycling test, in this test, the cells are run under a uniform rate up to 100 cycles, the rate set at 0.1 C rate, meaning it takes 10 hours to fully charge or discharge one cell. The specific capacity of the cells will be recorded to compare with the specific capacity in the first cycle to show the decay as the cycle number increases.

The second test is rate test, during this test, the cells will be run under different C rate it will start from 0.2 C rate for one full charge and discharge, meaning 5 hours for one full charge or discharge, and then 1 C rate for one full charge and discharge, meaning 1 hour for one full charge or discharge and then 3 C rate (20 minutes for one full charge or discharge), then 5 C rate (12 minutes for one full charge or discharge) and finally 10 C rate (6 minutes for one full charge or discharge).

Result and discussion

Materials characterization

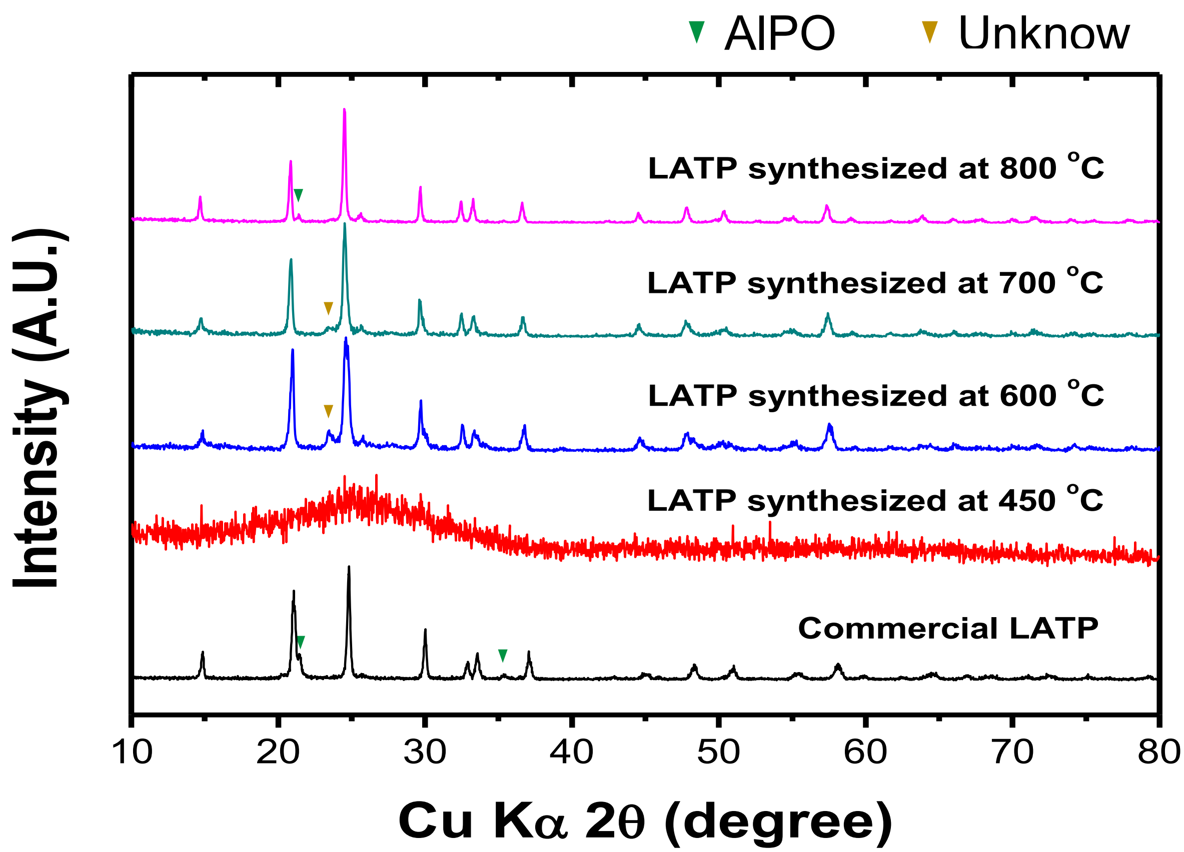

Figure 6, XRD patterns for LATP samples synthesized

When the LATP powder is acquired, it will be diagnosed by XRD to see if the pattern agrees with the common pattern of LATP so that researchers can ensure the LATP is ready to be used. As figure 6 shows, the pattern of the synthesized LATP agrees with the commercially used one, meaning they are completely the same and it is valid for research.

After the structure of LATP powder is checked as shown in Figure 7, SEM will be run on the sample of the powder to investigate the particle size and then distinguish the sample needs further process. As the figure shows, though the shape is irregular, the average diameter of the particle is within the range of 30~40 micrometers. As the concept that smaller sized particles allow more regular position addressing so that shorter paths for electron transmission, the LATP needs further processing to reduce its size. The ball milling method is chosen to proceed with the process. After the ball-milling process was conducted, SEM was taken again.

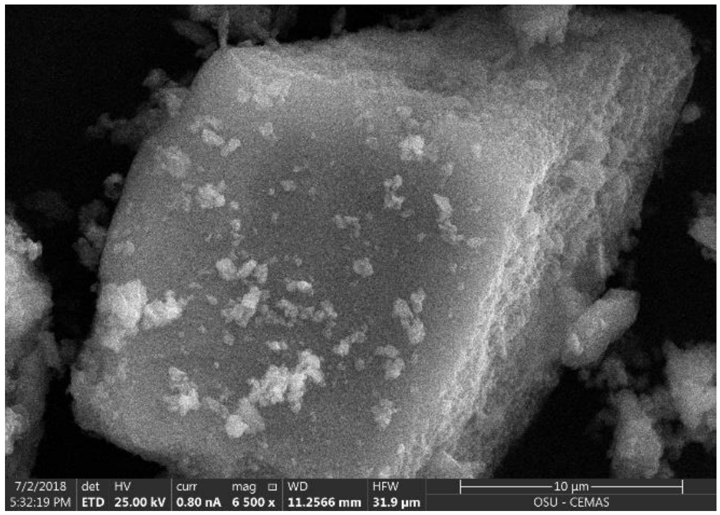

Figure 7. SEM results of LATP powder synthesized

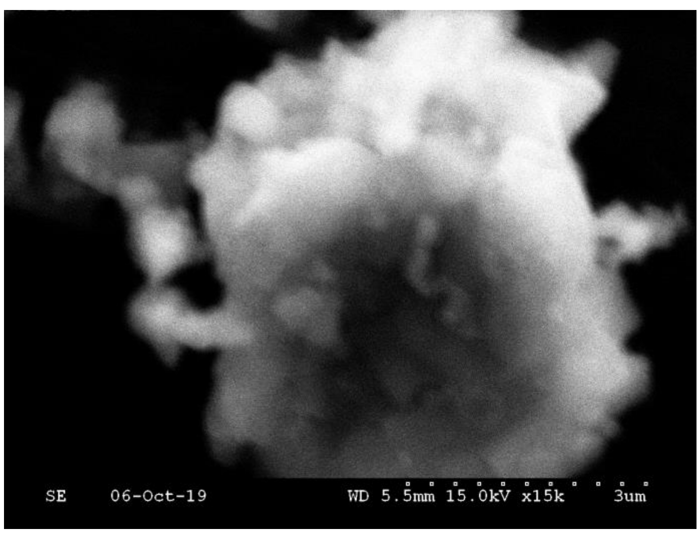

Figure 8. SEM results of LATP powder after ball milling

It is obvious that the diameter of the particles has been reduced to around 5 micrometers, which reaches the size of the NMC particle (average 5 μm), meaning the LATP powder is ready to be used after the LATP layer is deposited on the cathode layer, The images on the cross-section of the electrode were obtained to investigate the thickness of the layer of LATP plating thickness.

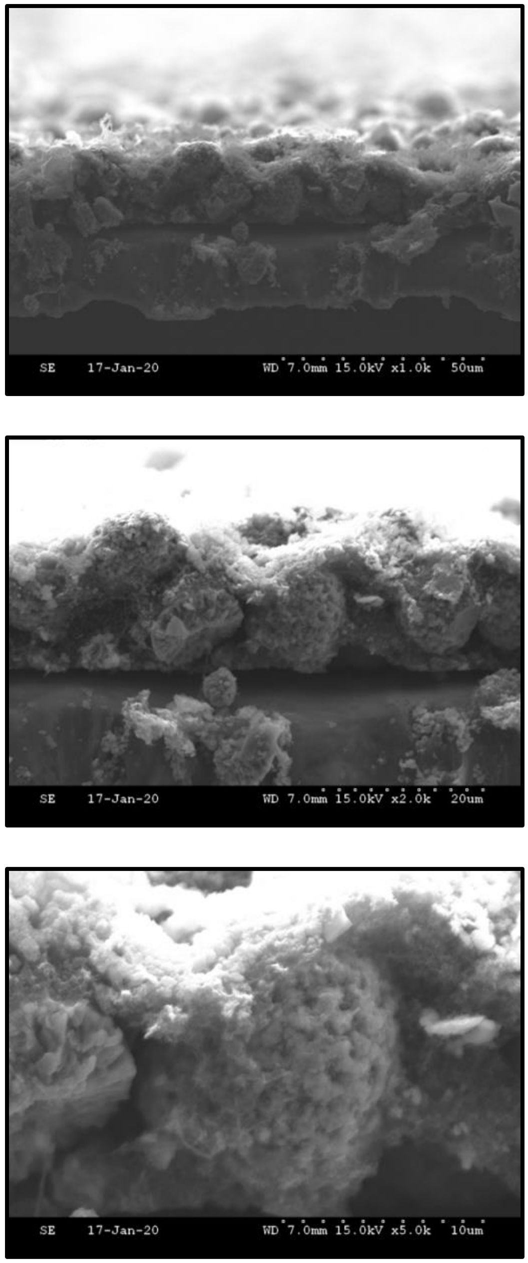

Figure 9. SEM image on cross-section of LATP plated NMC cathode.

Theoretically, the size of the NMC and LATP particles are both around 3-5μm in diameter. And since the LATP is shown white under SEM while NMC is shown black, what researchers expect are two separate layers with distinct black and white colors. As figure 9 shows, while what we can be seen from figure 9 is just one layer of particles, the other layer is missing. It was taken another SEM for pristine NMC for comparison.

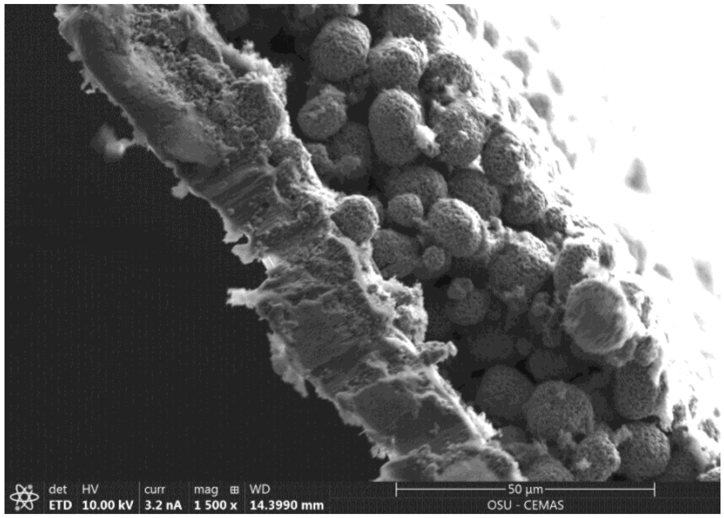

Figure 10. SEM of pristine NMC sample

From the shape of the particles, we determine the distinguished particles are NMC while the NMC particles are covered with extremely small, white particles. We assume the extremely small ones are LATP particles.

Electrochemical properties

The cycling test is the most frequently performed during the experiments since it directly examines the effect of mixing/coating on the electrochemical performances of cathodes.

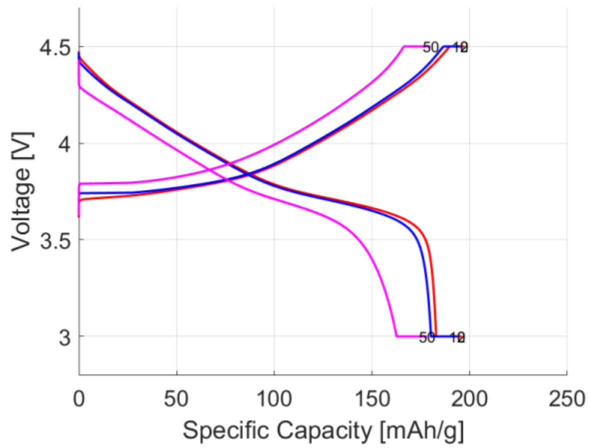

Figure 11. Cycling test result of pristine NMC cathode

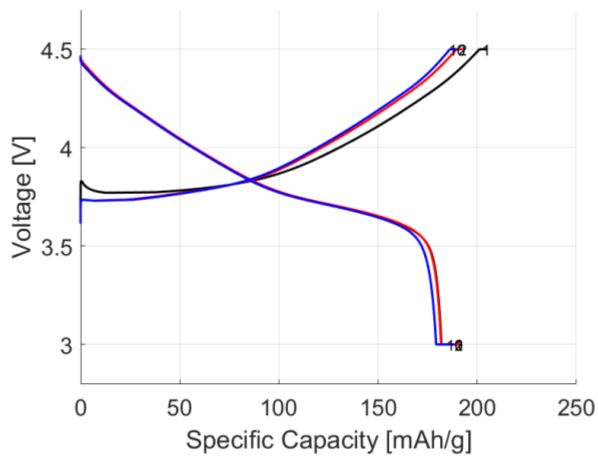

Figure 12. Cycling test result of LATP-NMC mixture (NMC: LATP = 3:1) cathode

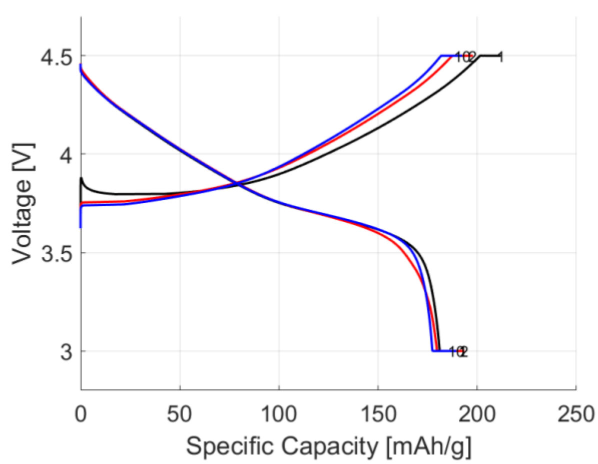

Figure 13. Cycling test result of LATP-NMC mixture (NMC:LATP = 1:1) cathode

As above figures show, the graphs are composed of two curves; the upward curve indicates the charging of the battery while the downward curve indicates the discharging process. As the first graph indicates, for pristine NMC cathode, there is a significant difference between the specific capacity of the first cycle and that of the 10th cycle, the difference grows even larger after the 50th cycle. This means, the decay of the pristine NMC cathode material is very obvious, it occurs massively at the beginning of the cycling.

While the results of the LATP-NMC mixture cathode show much more persistence, there is a smaller gap between the first cycle and the 10th cycle compared to the pristine NMC cathode, and there is barely any difference between the capacity of 10th cycle and that of the 50th cycle. It means there is still an obvious decay at the beginning of the cycling but during further cycling, the cathode shows much more robust and persistent performance.

for both mixture there are small gaps between capacities at different cycle numbers during charging, while the 1:1 mixture shows better performance, as the graph shows, the 3:1 mixture still has a distinguishable decrease between capacity at 10th cycle and that of 50th cycle, while the capacity curve of 1:1 mixture at 50th cycle covers the 10th cycle, meaning there is no difference on the capacity between 10th cycle and 50th cycle. So the 50% of LATP added is more optimum than 25% of LATP added in NMC for battery performance.

The LATP-plated NMC cathode shows even better performance than the LATP-NMC mixture.

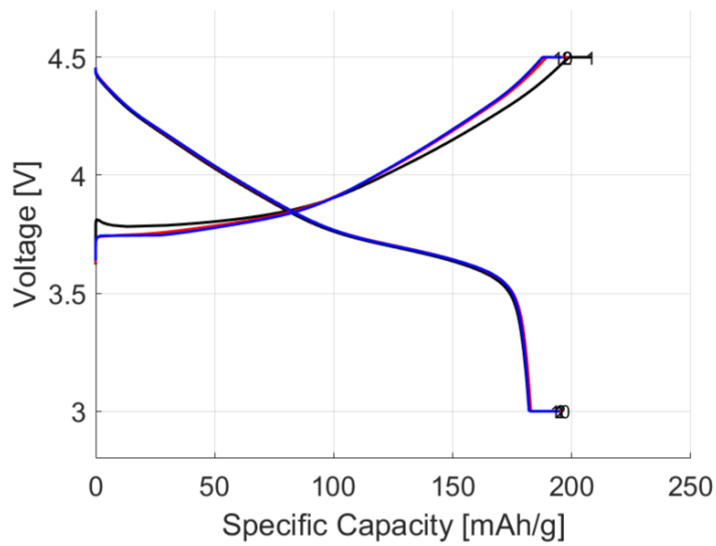

Figure 14. Cycling test result of LATP plated NMC cathode

As the figure 19 shows, there is still a difference between the capacity at 10th cycle and the capacity at first cycle during the charging process, but there is almost no difference between capacity at 10th cycle and that at 50th cycle, meaning the plated cathode is even more robust than the mixture cathode. Furthermore, among the discharging curves, there is literally no difference between three curves, meaning there is no difference between capacities at the first cycle and at the 10th cycle and at the 50th cycle. It shows that there is no decay of cathode before the first 50 full charging-discharging cycles. The robustness of the battery is further improved.

Figure 20 shows the discharge capacities of each cathode materials up to 300 cycles. All the cell was tested in the voltage range from 3V to 4.5V at room temperature (25 oC). Both mixed and plated samples showed more discharge capacities than the pristine NMC cathode up to around the 300th cycle. This claims it is obvious that both ways help to improve the cycle-abilities.

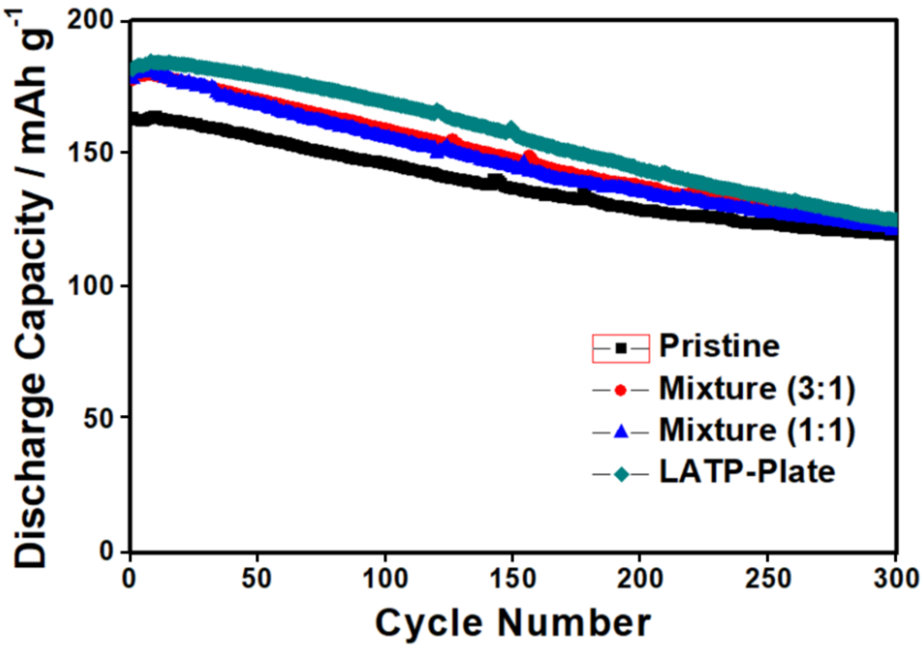

Figure 15. Discharge capacities of the (black) pristine, (red and blue) LATP-mixed, (olive) LATP-plated NMC cathodes

As the cycling test indicates the life of the battery, the rate test indicates the capability of batteries under different power demanding, another significant property of the battery.

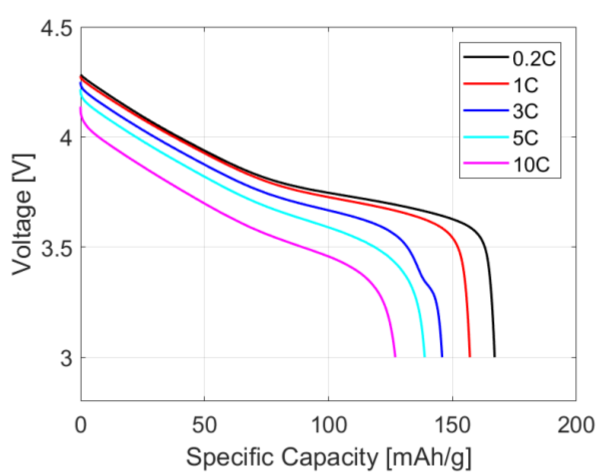

Figure 16. Rate test result of pristine NMC cathode

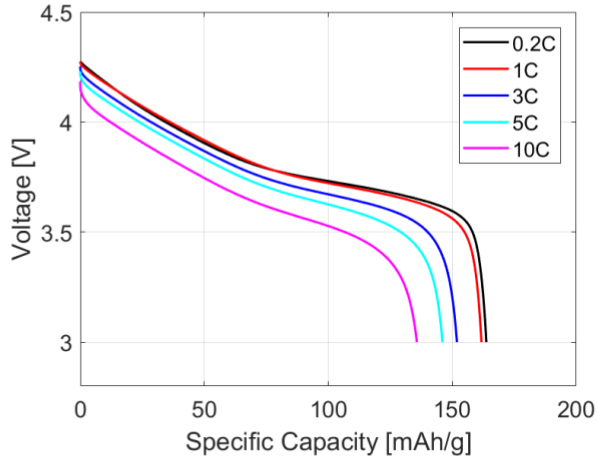

Figure 17. Rate test result of LATP-NMC mixture (NMC: LATP = 3:1) cathode

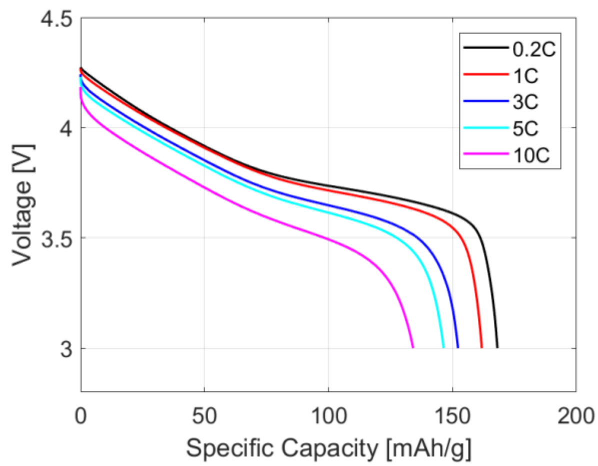

Figure 18. Rate test result of LATP-NMC mixture (NMC: LATP = 1:1) cathode

As the first figure shows, as the charging-discharging rate increases, the capacity of the battery decreases significantly. For the batteries made from the mixture cathodes, the decrease is also significant and the specific capacities under low rate (0.2 C, fully charging or discharging using 5 hours) have no improvement compared to the battery made from the pristine NMC cathode. However, there are improvements in performance under the high charging-discharging rate.

For example, under 3 C rate (fully charging or discharging using 20 min), the specific capacity of the pristine NMC cathode is around 145 mAh/mg while the LATP-NMC mixture (NMC: LATP =

3:1) has the capacity of 152 mAh/g, the other LATP-NMC mixture (NMC: LATP = 1:1) mixture cathode 151 mAh/g. the difference between the specific capacity increases as the charging-discharging rate increases, under 10 C rate (fully charging or discharging using 6 min), the specific capacity of the pristine NMC cathode is around 124 mAh/mg while the LATP-NMC mixture (NMC: LATP = 3:1) cathode has the capacity of 135 mAh/g, the other LATP-NMC mixture (NMC: LATP = 1:1) mixture cathode 134 mAh/g, it is almost a 10% improvement.

the LATP plated NMC cathode shows even better results in rate test which achieved a total improvement on all the rates tested.

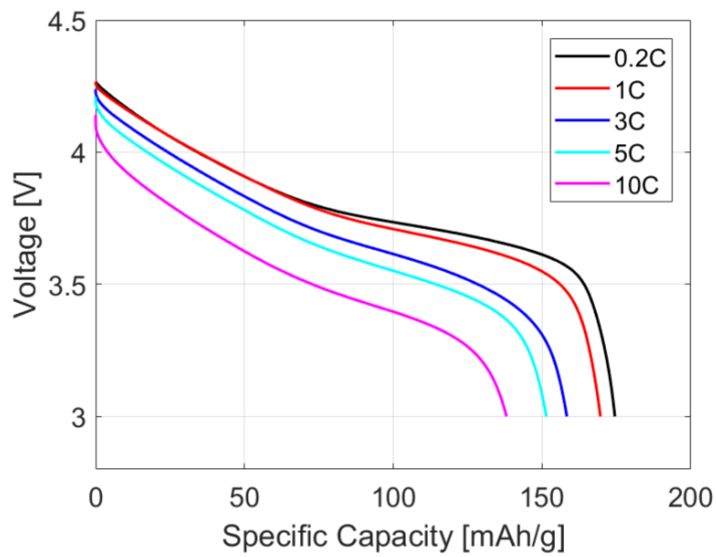

Figure 19. Rate test result of LATP plated NMC cathode

As the figure shows, compared to the rate test result of pristine NMC cathode, all the curves move rightwards, it means that the specific capacity of the battery increases regardless of the charging-discharging rate. Specifically, under 5 C rate, the specific capacity of the battery surpasses 150 mAh/g, compared to the same value from the test result of pristine NMC cathode, which is around 135 mAh/g, it improves more than 10%. Under 10 C rate, the specific capacity of the battery reaches 140 mAh/g, compared to the same value from the test result of pristine NMC cathode, which is around 120mAh/g, it improves the capacity by around 16%.

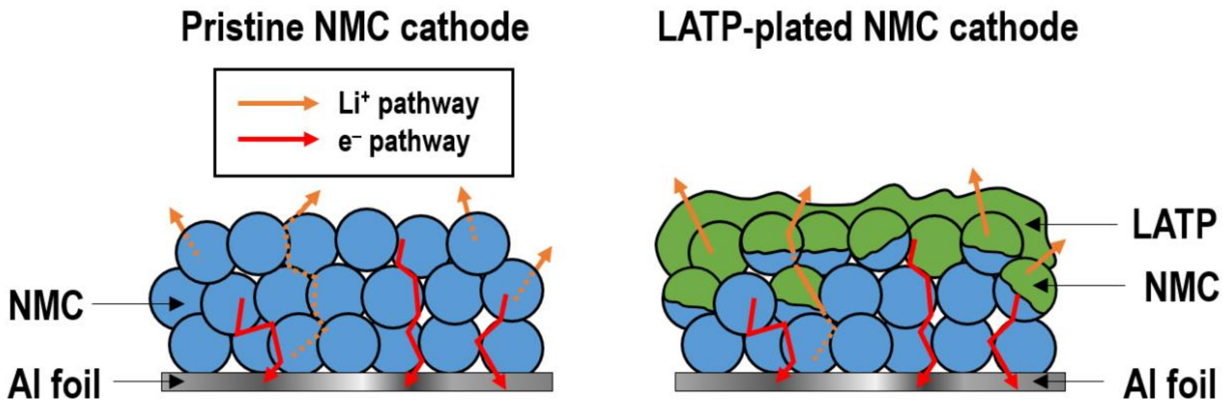

Figure 20. Schematic image for explanation of Li-ion behavior in (left) pristine NMC cathode and (right) LATP-plated NMC cathode

LATP has around 10^{-4} S/cm of Li-ion conductivity, which is much bigger than the conductivity of NMC. In a cell, both electronic and ionic transfer is crucial. For the fast electron transfer, carbon additive is typically put into the cathode. As shown in Fig. 25, Li-ions can be intercalated/deintercalated from the cathode material, and the extracted Li-ion will naturally find the fastest route in the cathode. Therefore, it is assumed that the extracted Li^{+} will pass through the surface of the Li-ionic conductive LATP, which accelerates the migration of the Li-ions. In addition, it is properly assumed that the LATP layer plays as a passivating layer on the cathode, which enhances the cycle-abilities. The same assumption will be applied in the mixed cathode sample.

Conclusion

The results of both cycling test and rate-capability tests show promising improvements by adding LATP as a high Li-ion conductive material. almost all the samples showed enhanced performances. Among all the improving methods, the plating method is the most optimum way since the plating method shows an especially positive effect on battery performance. Even under such experimental circumstances without careful design or control, the improvement can be virtually astonishing which shows the great potential of coating on the battery industry. With further study on the materials and plating thickness, it will surely be more valuable.

Future work

The research will continue to investigate the thickness of the coating layer since, during the previous experiments, plating has already been proved the most optimum coating method. The research will also investigate the melting mechanism of the LATP layer happened in the plating process, so far from the testing data, whatever the melting causes, it seems to be beneficial to the battery performance. With further study on this melting reaction, it might offer another perspective on the battery industry.

Appendix

Appendix A: XRD

XRD is an abridgment of X-ray Powder Differentiation. It is an analytical method used to identify the structure and compositions of crystalline materials. The concept of XRD basically follows the diffraction of X-ray. Atoms in the periodic crystal lattice are defined and three-dimensional arrangement of particles. as the X-ray hit the atom layers, diffraction occurs, and the specific diffraction follows the equation:

$$n\lambda = 2d\sin\theta$$

in this equation, n represents the reflection order, λ represents the wavelength of x-rays emitted, d represents the characteristic spacing between atomic layers inside crystalline materials, and θ is the angle of diffraction.

by theory, every element has unique θ after diffraction, therefore, by detecting the value of θ, the composition of the material can be identified.

Appendix B: SEM

SEM is the abridgment of the Scanning Electron Microscope. It is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations.[11] before the SEM starts, the sample will be conducted with Au-Pd coating to acquire better electron conductivity, the electron will then be shot on the sample and their movement along the sample surface will be traced to show the image.

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